The Ultraviolet Spectra of Some Polysilanes[1]

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A recent article[2] prompts us to report some results of our own studies on p_π-d_π bonding in polysilanes. Although the literature contains several references to the participation of 3d orbitals fo silicon to effect enhanced bonding in phenyl[3] or vinyl-substituted silanes,[4] the investigation of this kind of participation has not been extended to the spectral study.

Ultraviolet spectroscopic investigations, however, afford an obvious source of information concerning the electronic levels of these molecules, and will serve to provide an important criterion for the existence of dative p_π-d_π bonding.

During the course of our study of the properties of silicon-silicon bonding, it has been found that polysilanes with a phenyl or vinyl group have a very intense absorption in the ultraviolet region, unlike phenyltrimethylsilane[5] and vinyltrimethylsilane.[6]

The absorption spectra of some phenyl or vinyl substituted disilanes and trisilanes in *n*-hexane were studied in the ultraviolet region, 210~260 mμ; the experimental results are presented in Table I. Hexamethyldisilane, the

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[1] Presented in part at the Symposium of Organometallic Chemistry, Nagoya, October 13, 1963.

[2] H. Gilman, W. H. Atwell and G. L. Schwebke, *Chem. & Ind.*, **1964**, 1063.

[3] C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London (1960), Chap. 3.

[4] J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 487, 2870 (1963); J. J. Eisch and R. T. Beuhler, ibid., **28**, 2876 (1963).

[5] K. Bowden and E. A. Braude, *J. Chem. Soc.*, **1952**, 1068.

[6] C. E. Scott and C. C. Price, *J. Am. Chem. Soc.*, **81**, 2670 (1959).

parent compound, was found to have no absorption in this region.

Recently, Hague and Prince[7] have reported an intense absorption at 246.5 mμ for hexaphenyldisilane. They described this absorption as an interaction between phenyl groups through the silicon-silicon bond. However, judging from the table, apparently the most striking red shift in the absorption maxima is observed for phenylpentamethyldisilane; namely, the introduction of a pentamethyldisilyl group into benzene causes a red shift to the extent of 28 mμ in the 200 mμ-band.[8]

TABLE I. UV SPECTRA OF SOME POLYSILANES

Polysilane	λ_{max} mμ	ε_{max}
$PhSiMe_2SiMe_3$	231.0	10900
$PhSiMe_2SiMe_2Ph$	238.0	18500
$Ph_2SiMeSiMePh_2$	240.0	25900
CH_2=CH-$SiMe_2SiMe_3$	223.2	5200
CH_2=CH-$SiMe_2SiMe_2$-CH=CH_2	227.0	9790
$PhSiMe_2SiMe_2SiMe_3$	240.0	15400
	221.3	13000
$Me_3SiSiMePhSiMe_3$	243.0	13000

Therefore, the evidence thus obtained suggests that the pentamethyldisilyl group can interact directly with the phenyl group, possibly by p_π-d_π conjugation. A rather small shift in the absorption maxima can be found when a second phenyl group is introduced into phenylpentamethyldisilane at the vicinal position, while the absorption intensity increases. Almost the same trends are observed for vinylpentamethyldisilane and divinyltetramethyldisilane.

Since the trimethylsilyl group has only a small bathochromic effect on benzene[5] or ethylene,[6] it seems reasonable to assume that the silicon-silicon bond is essential as a chromophore to make an enhanced conjugation with benzene or ethylene.

Further details will be published later.

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[7] D. N. Hague and R. H. Prince, *Proc. Chem. Soc.*, 300 (1962).

[8] Fine structures in the 260 mμ-band are almost masked by the strong absorption near 235 mμ in phenyl-substituted polysilanes.